RESTRICTED ROTATION IN ARYL OLEFINS AND IN IMINO ETHERS

BY

ROBERT ISRAEL MELTZER

B.S., College of City of New York, 1939
M.S., Ohio State University, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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Introduction

The many compounds synthesized in the biphenyl series have resulted in a good understanding of the phenomenon of restricted rotation in this class of compounds. Adams and coworkers have extended the theories from the biphenyls to the aryl olefins. The object of this research was to investigate diaryl olefins and benzalimines with respect to restricted rotation.

Experimental and Discussion of Results

Acetomesitylene pinacol was prepared by the electrolytic reduction of acetomesitylene by the method of Swann.[1] The pinacol was converted to 2,3-dimesityl-2-butene in three ways. The first two methods required the preliminary dehydration of the pinacol to 2,3-dimesitylbutadiene by treatment with acetyl chloride.[1] By one method the latter compound was reduced by hydrogen at high pressure over Raney nickel. In the second method hydrogen bromide was added to the butadiene and the bromine in the resulting compound was replaced by hydrogen by the action of zinc and acetic acid. The third method of preparing 2,3-dimesityl-2-butene was by the treatment of the pinacol with hydroiodic acid in glacial acetic acid solution. The product by all three methods was the same. The methods of synthesis constitute the main proof of structure of the compound.

Ultraviolet absorption spectra were taken of 2,3-dimesityl-2-butene and of 1,2-dimesitylethylene prepared from the corresponding glycol by treatment with hydroiodic acid. The spectra showed that although both have one peak of absorption at approximately the same wavelength, the ethylene compound has an additional region of absorption. This result would be expected if free rotation were not possible about the aryl-olefin bond in 2,3-dimesityl-2-butene.[2]

If restricted rotation about the aryl-olefin bond does exist, and if the mesityl groups of one form of 2,3-dimesityl-2-butene are substituted with one substituent each, then two forms of 2,3-*bis*-(monosubstituted mesityl)-2-butene should exist. The substituents introduced by this worker were bromo, nitro, and sulfonyl chloride. In all three cases only one form of the compound was obtained. This result may be accounted for by either the lack of restricted rotation or by the entrance of the substituents into the molecules in only one way in each case. This experimenter favors the latter explanation. Furthermore if restricted rotation is present in the molecule, one of the possible forms should be optically active. The strychnine salt of 2,3-*bis*-(mesitylsulfonic acid)-2-butene was prepared. No indication of optical isomerism was obtained and it is, therefore, assumed that the product is the meso isomer.

In the benzalimine series the compound studied was N-phenylbromomesitimino-*p*-carboxyphenyl ether. This compound was prepared by a method similar to the one used by Chapman[3] for the preparation of imino ethers. Bromomesitanilide imino chloride was treated with an ether solution of sodium ethylate and ethyl *p*-hydroxybenzoate. The resulting N-phenylbromomesitimino-*p*-carbethoxyphenyl ether was hydrolyzed to the free acid by treatment with alcoholic sodium hydroxide. The *d*-α-phenylethylamine and the *d*-quinine salts were prepared. Only one form of each was found to exist. The quinine salt showed no sign of mutarotation in boiling *n*-butanol. The probability is that restricted rotation does not exist in this molecule.

Summary

The preparation of 2,3-dimesityl-2-butene was carried out in three ways. Absorption spectra support belief in the presence of restricted rotation in the molecule. The dibromo, the dinitro, and the sulfonyl chloride derivatives of the

compound were prepared and each was obtained in one form only. The strychnine salt of 2,3-*bis*-(mesitylsulfonic acid)-2-butene was prepared and only one form was isolated.

N-Phenylbromomesitimino-*p*-carboxyphenyl ether was prepared. Its *d*-α-phenylethylamine and its *d*-quinine salts showed no sign of diastereoisomerism.

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VITA

The writer was born in New York City on October 4, 1918. He attended the public schools of that city and was graduated from DeWitt Clinton High School in 1935. In 1939 the College of the City of New York granted him the degree of Bachelor of Science and in the following year the Ohio State University conferred upon him the degree of Master of Science. He enrolled at the University of Illinois in 1940. He was a teaching assistant in chemistry during the years 1941-1943.

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